

## **WET ETCH OF TITANIUM-TUNGSTEN FILM**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application is related to co-pending U.S. Application No. 09/226,996, filed January 7, 1999, which is a continuation of U.S. Application No. 09/043,505, filed March 23, 1998, now U.S. Patent No. 6,117,783, which claims the priority of International Patent Application No. PCT/US97/12220 filed July 21, 1997, which in turn claims the priority of U.S. Provisional Application Serial No. 60/023,299, filed July 26, 1996, the disclosures of each of which are incorporated in their entirety by express reference hereto.

### **FIELD OF THE INVENTION**

[0002] This invention relates to an improved composition and process for the chemical mechanical polishing or planarization of semiconductor wafers. More particularly, it relates to such a composition and process which are tailored to meet more stringent requirements of advanced integrated circuit fabrication.

### **BACKGROUND OF THE INVENTION**

[0003] Chemical mechanical polishing (or planarization) (CMP) is a rapidly growing segment of the semiconductor industry. CMP provides global planarization on the wafer surface (millimeters in area instead of the usual nanometer dimensions). This planarity improves the coverage of the wafer with dielectrics (insulators) and metal substrates and increases lithography, etching, and deposition process latitudes. Numerous equipment companies and consumables producers (slurries, polishing pads, etc.) have now entered the market.

[0004] CMP has been evolving for the last two decades and has been adapted for the planarization of inter-layer dielectrics (ILD) and for multilayered metal (MLM) structures. During the 1980s, IBM developed the fundamentals for the CMP process. Previously (and still used in many fabs today), plasma etching or reactive ion etching (PIE), SOG ("spin on glass"), or reflow, *e.g.*, with boron phosphorous spin on glass (BPSG), were the only methods

for achieving some type of local planarization. Global planarization deals with the entire chip, while “local” planarization normally only covers a  $\sim 50$  micron<sup>2</sup> area.

[0005] At the 1991 VMIC Conference in Santa Clara, CA., IBM presented the first data about CMP processes. In 1993, at the VMIC Conference, IBM showed that a copper damascene (laying metal lines in an insulator trench) process was feasible for the MLM requirements with CMP processing steps. In 1995, the first tungsten polishing slurry was commercialized.

[0006] The National Technology Roadmap for the Semiconductor Industries (1994) predicted that computer chips with 0.35 micron feature sizes would be reduced to 0.18 micron feature size in 2001. The DRAM chip was projected to have a memory of 1 gigabit, and a typical CPU was projected to have 13 million transistors/cm<sup>2</sup> (at the time, they only contained 4 million). The number of metal layers (the “wires”) was projected to increase from the current 2-3 to 5-6, and the operating frequency, which was then 200 MHz, was projected to increase to 500 MHz. These projections indicated an increase in the need for a three dimensional construction on the wafer chip to reduce delays of the electrical signals. Chip designs have changed from about 840 meters of “wires”/chip to having as much as 10,000 meters of “wires”/chip or more (without any significant design changes) in the near future. This length of wire can severely compromise the chip’s speed performance.

[0007] The global planarization required for today’s wafer CDs (critical dimensions) improves the depth of focus, resulting in better thin metal film deposition and step coverage and subsequently increases wafer yields and lowers the cost/device. It was estimated (1996) that it cost  $\sim \$114$ /layer/wafer with then-existing limited planarization processes. As the geometries have become smaller than 0.35 microns, the planarity requirements for better lithography have become more critical. CMP is becoming more important, if not essential, for multiple metal levels and damascene processes.

[0008] The CMP process would appear to be the simple rotation of a wafer on a rotary platen in the presence of a polishing medium and a polishing pad that grinds (chips away) the surface material. The CMP process is actually considered to be a two part mechanism: first, chemically modifying the surface of the material; and then removing the altered material by mechanical grinding. The challenge of the process is to control the chemical attack of the substrate and the rate of the grinding and yet maintain a high selectivity (preference) for

removing the offending wafer features without significant damage to the desired features. The CMP process is very much like a controlled corrosion process.

[0009] An added complexity is that the wafer is actually a complex sandwich of materials with widely differing mechanical, electrical and chemical characteristics, all built on an extremely thin substrate that is generally flexible.

[0010] The CMP processes are very sensitive to structural pattern density, which will affect metal structure “dishing” and oxide erosion. Large area features are typically planarized slower than small area features.

[0011] At the 1995 SEMICON/Southwest Technical program on CMP, it was stated that “Metal CMP has an opportunity to become the principal process for conductor definition in deep submicron integrated circuits.” Whether or not it has depends on one’s assessment of the relative success of CMP technologists in achieving the successful integrated process flow at competitive cost.

### Slurries

[0012] CMP has been successfully applied to the planarization of interdielectric levels (IDL) of silicon oxides, BPSG, silicon nitride, and also metal films. The metal films currently being studied include tungsten (W), aluminum (Al), and copper (Cu).

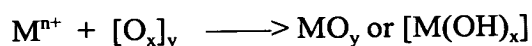
[0013] The polishing slurries are a critical part of the CMP process. The polishing slurries generally have an abrasive suspension (silica, alumina, etc.) usually in a water solution. The type and size of the abrasive, the solution pH and presence of (or lack of) oxidizing chemistry are very important to the success of the CMP process.

[0014] Metal CMP slurries must have a high selectivity for removing the unwanted metal compared to the dielectric features on the wafers. The metal removal rate should typically be between 1700 to 3500 Å/min, without excessive “dishing” of the metal plugs or erosion of the oxide substrate.

[0015] The oxide CMP has similar requirements and polishing rates generally close to 1700 Å/minute.

## Metal Polishing

[0016] This type of polishing relies on the oxidation of the metal surface and the subsequent abrasion of the oxide surface with an emulsion slurry. In this mechanism, the chemistry's pH is important. The general equations are (M = metal atom):



[0017] Under ideal conditions, the rate of metal oxide ( $MO_y$ ) formation ( $V_f$ ) will equal the rate of oxide polishing ( $V_p$ ), ( $V_f = V_p$ ). If the pH is too low (acidic), then the chemistry can rapidly penetrate the oxide and attack the metal ( $V_f = V_p$ ), thus exposing the metal without any further oxide formation. This means that all metal surfaces, at high points and in valleys, are removed at the same rate. Planarization of the surface is not achieved. This could cause metal plug connectors to be recessed below ("dishing") the planarization surface, which will lead eventually to poor step coverage and possible poor contact resistance.

[0018] When the pH is too high (caustic), then the oxide layer may become impenetrable to the chemistry, the metal becomes passive ( $V_f = V_p$ ), and the metal polishing rate becomes slow. Metal polishing selectivity to oxide generally ranges from 20 to 100:1, depending on the metal type. Tungsten metal should have selectivities >50:1 for the metal to oxide, and copper could have >140:1 metal to oxide selectivity. Etch rates can be up to 7000 Å/min. The chemical diffusion rate and the type of metal oxide surface are important to the successful planarization process. A detailed mechanism has been proposed by Kaufman.

[0019] In practice, the low pH and highly corrosive oxidants (ferric nitrate) being used with an example metal CMP process has created corrosion problems with the polishing equipment. Currently the oxidant used in the metal polishing step has ranged from nitric acid to hydrogen peroxide, cesium and ferric nitrate solutions, and even ferric cyanide solutions. Because of chemical stability problems, many slurries are made up at the point of use, which means that there is little or no shelf life.

[0020] Metal planarization needs an oxidizing reagent that is stable and is not going to contribute to mobile ion contamination, will not "stain" the equipment, will not affect the slurry composition and slurry particle distribution, and is generally environmentally friendly.

The current hydrogen peroxide systems are not stable when premixed with the slurry and therefore have to be delivered to the polishing equipment with separate pumping systems and mixed at the point of use. The ferric nitrate system requires a low pH and is known to “stain” the polishing equipment. The potassium iodate system also requires special handling.

[0021] An emerging area of CMP will deal with the copper damascene process. The copper metal interconnects (wires) will be required because of its better conductivity compared to Al. One major disadvantage with copper is its easy diffusion through silica under normal operating conditions. The copper damascene process will need barrier layers to prevent this copper diffusion.

[0022] In the damascene process, “lines” or trenches are etched into the interdielectric layers, and then the walls of these trenches are coated with barrier materials. These materials can be composed of Ta, TaN, Ti, or TiN, among other materials. Copper metal is then deposited, by electroless or electrode plating, or by PVD or CVD methods. The excess copper above the trench is then removed by chemical mechanical polishing. The difficult part of the CMP process is not to remove excess copper (“dishing”) which will remove the copper metal below the interdielectric layer.

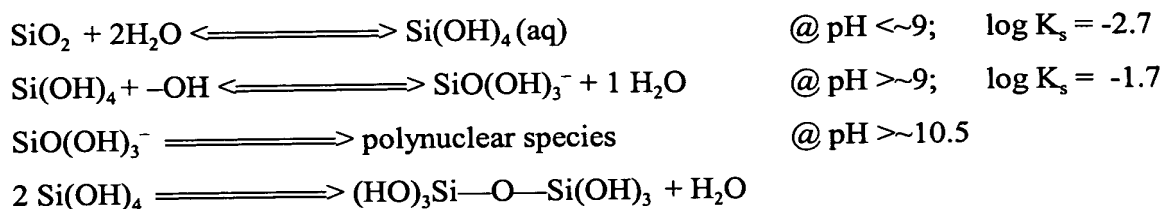
[0023] CMP of the copper metal can be done over a wide pH range (2 to 12). Pourbaix diagrams for copper indicate that copper can only be passivated (oxide layer) in neutral or basic solutions. In acid solutions an inhibitor, *e.g.*, benzotriazole (BTA), is usually needed to control the isotropic etching effects from the chemistries used in the CMP process. Much of the CMP work has been done with hydrogen peroxide at various pH ranges.

[0024] Some CMP work has been done with ammonium hydroxide, because of its ability to form copper complexes though there are problems with poor selectivity between copper and titanium and silicon oxide.

#### Interlayer Dielectric (Oxide) Polishing

[0025] A while ago, a group of engineers using ILD (oxide) CMP was asked to prioritize CMP processing requirements. The major concern was surface damage (scratching, etc.), followed by wafer (polishing) nonuniformity (within wafer and wafer to wafer), then polishing rate, and finally planarity. For silica, the mechanisms are still being developed, but the polishing process appears to involve two concurrent processes; a mechanical process

involving plastic deformation of the surface, and chemical attack by hydroxide (-OH) to form silanol bonds.



[0026] In a slurry (colloidal suspension) the pH is important and for the silicon oxide system it needs to be in the 10 to 11.5 range. CMP users have frequently used silicon oxide-based slurries which used to be “buffered” with sodium hydroxide but have more recently been formulated with potassium or ammonium hydroxide solutions. Etch rates can be in the range of 1700 Å/min.

[0027] If the pH is too high the polynuclear species may start to precipitate in an unpredictable manner. There is also the possibility of a condensation process to form Si bonds.

[0028] There are other important features of the silicon surface that will influence the etch rates and final surface conditions, *e.g.*, metal contamination and possibly micro scratches. As mentioned above, the typical silicon surface is terminated (covered) with -OH groups under neutral or basic conditions. The silicon surface is hydrophilic (“wetable”). These groups activate the surface to a number of possible chemical or physioabsorption phenomena. The Si-OH groups impart a weak acid effect which allows for the formation of salts and to exchange the proton (H<sup>+</sup>) for various metals (similar to ion exchange resins). These Si-O<sup>-</sup> and Si-OH groups can also act as ligands for complexing Al, Fe, Cu, Sn, and Ca. Of course the surface is very dipolar, and so electrostatic charges can accumulate or be dissipated depending on the bulk solution’s pH, ion concentration, and charge. This accumulated surface charge can be measured as the Zeta potential.

[0029] If the silica (Si) surface underneath the oxide layer is exposed because of an over aggressive polishing process, this could cause electrochemical problems because of a modest redox potential which will allow Cu, Au, Pt, Pb, Hg and Ag to “plate on” the surface.

Exposure to light will also affect the redox reaction for Cu. The light will “generate” electrons in the semiconductor material, which then reduces the copper ion to Cu°.

### Post-Clean Processes

[0030] Both the ILD and metal polishing processes must eventually pass through a final cleaning step to remove traces of slurry and the chemistry. Though the process appears to be simple, *e.g.*, a brush scrub and a rinse cycle, considerable effort is being expended to determine if the process should involve either single side, double sided scrubbing, single wafer or batch processing, spray tools or even immersion tanks. One engineering group working with post-clean CMP ranked wafer cleanliness (from slurry and pad particles and metallic contamination) as the most important issue in the post-clean step. Process reliability and defect metrology were other important areas of concern.

[0031] Residual particle levels should be ~1 particle/20cm<sup>2</sup>, with 90% of these particles having less than 0.2 micron size. Line widths of 0.35 micron require the removal of particles down to 0.035 microns or less. Incomplete particle removal is believed decrease wafer yield. Low defect (scratches) levels and acceptable planarity can also be very important.

[0032] Most fabs have developed their own in-house technology for the post-clean CMP steps. Most of the “chemistries” involve DI water with either added ammonium hydroxide or HF, while some fabs are using the standard RCA SC-1 (NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O) and SC-2 (HCl:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O) cleaning steps traditionally used in the front end process.

[0033] There are five mechanisms for removing impurities (particles and/or ions) from wafer surfaces:

- Physical desorption by solvents: Replacing a small number of strongly absorbed material with a large volume of weakly adsorbed solvent (changing the interaction of the surface charges).
- Change the surface charge with either acids or bases: The Si-OH or M-OH group can be protonated (made positive) in acid or made negative with bases by removing the proton.
- Ion competition: Removing adsorbed metal ions by adding acid (*e.g.*, ion exchange).

- Oxidation or decomposition of impurities: Oxidation of metals, organic materials or the surface of slurry particles will change the chemical bonds between the impurities and substrate surface. The chemical reaction can either be through redox chemistry or free radicals.
- Etching the surface: The impurity and a certain thickness of the substrate surface is dissolved.

### Periodic Acid Chemistries for CMP

[0034] Precision layering of the integrated circuit structure requires that excess materials from the previous manufacturing step be removed from the clean substrate. The CMP process removes the excess material through a wet chemical etch of the surface material followed by a mechanical abrasion of the etched surface. As such, CMP is like a controlled corrosion, and chemical selectivity is essential to maintaining desired intricate features on the substrate. An example is the copper damascene process, where trenches are etched into interdielectric layers, the walls of the trenches are coated with barrier materials, and then copper is deposited into the trench to serve as the conductive material. Excess copper above the trench is then removed by CMP. The challenge in CMP is always to remove the excess material evenly without “dishing” and creating poor contact between layers. Interlayer dielectrics can be polished in this manner also. A patent that explains CMP is U.S. Patent No. 6,117,783. Spin-etch CMP is a preferred embodiment in conjunction with the present invention, since foam treatment mediums would most benefit this process. Although spin-etch procedures vary in the manner in which the substrate is spun, whether mounted to a chuck through an insulating layer or allowed to spin free on a pad of nitrogen gas, the goal in either case is to apply an etching composition to the substrate with controlled and even pressure to globally plane the substrate with precision.

[0035] The use of periodic acid ( $H_5IO_6$ ), an oxidant, with deionized water to serve as an etching agent for spin-etch CMP, is disclosed in co-pending U.S. Application No. 10/060,109, filed January 28, 2002. Caustics such as potassium hydroxide, sodium hydroxide, or metal free caustics such as ammonium hydroxide, tetramethylammonium hydroxide (TMAH), 2-hydroxyethyl-trimethylammonium (choline) hydroxide, and choline salt derivatives can be added to adjust the pH. The following example is from U.S. Pat. No.



6,117,783 and shows the effect of pH when using periodic acid. Removal rates of tungsten generally increase with pH for periodic acid in water on 3" wafers coated with sputtered tungsten using 1% or 2.5% alumina and 0-3 parts ammonium hydroxide to adjust pH. Periodic acid was added to an alumina slurry at a rate of 50-100 mL/min, and the wafers were polished using a Logitech PM5 polisher (33 rpm, 12" IC1000 pad, 2 psig), as shown below in Table 1:

TABLE 1. EFFECT OF pH ON ETCHING WITH PERIODIC ACID

Alumina	Periodic Acid	pH	Removal Rate
(parts per 100)	(parts per 100)		(Angstrom/min)
1.0	2.0	1.4	130
1.0	2.0	1.9	274
1.0	2.0	2.1	326
2.5	2.0	2.1	252
2.5	2.0	6.8	426

[0036] The above table shows that periodic acid etches metals and that the etch rate can be controlled by adjusting the pH of the periodic acid and alumina slurry. The pH can be adjusted by inorganic bases such as KOH and NaOH, or metal-free organic bases such as TMAH, choline salts, and choline salt derivatives.

#### Etching and residue removal of TiW alloy

[0037] Titanium or titanium alloys are extensively used for barrier or adhesion layer in wafers. Common titanium metals used for this purpose include titanium (Ti), titanium nitride (TiN), titanium tungsten (TiW), and the like.

[0038] To remove these titanium metals and their etching residues, a method involving hydrogen peroxide ( $H_2O_2$ ) is most widely used. Typically, a solution containing 30%  $H_2O_2$ , with a pH of about 3 to 4, is used in a process involving a megasonic transducer. Wafers are processed for an appropriate length of time, rinsed, and then rotated. A similar process is then repeated a second time. The second process is necessary because the megasonic pattern used for the etching and removing the titanium metals cannot completely encompass the whole wafer in one pass.

[0039] Occasionally, it is possible for the operators to skip the second pass, thus resulting in a wafer with a lot of residue. Moreover, incomplete removal of residues, *e.g.*, TiO<sub>2</sub>, organometallic residues, metals, etc., can result even with a two pass process. Therefore, it would be advantageous to have a one pass process that can effectively etch and remove the titanium metals and their residues, while not harming Al, Cu, or an AlCu alloy layer.

## SUMMARY OF THE INVENTION

[0040] One aspect of the invention relates to a composition containing water and between about 2.5% and 30% by weight of periodic acid, alternately from about 5% to about 20%, from about 7.5% to about 15%, from about 8% to about 12%, or of about 10% by weight. This composition can advantageously be effective in removing a TiW alloy and removing residues of etching of TiW alloy, while preferably removing a relatively small amount of Al, Cu, or an AlCu alloy. In a preferred embodiment, the pH of the composition is less than 7, alternately less than about 4 or less than about 2.

[0041] In one embodiment, the composition can be substantially free of hydrofluoric acid. In another preferred embodiment, the amount of periodic acid can be about 10% by weight of the composition.

[0042] Another aspect of the invention relates to a method of etching and cleaning a TiW alloy layer that includes: providing a substrate comprising an exposed TiW alloy layer; etching the TiW alloy by a method which results in formation of etching residue; contacting the substrate with the composition according to the invention for a time and at a temperature sufficient to cause the composition to remove at least a portion of the TiW alloy and substantially all of the etching residue from the substrate; and rinsing the substrate.

[0043] In one embodiment, the substrate can further include an exposed AlCu alloy, and preferably the specificity of removal of TiW to AlCu, in terms of etch rate, is at least about 3, alternately at least about 5 or at least about 7. In another embodiment, the temperature at which the solution is used can range from about 20°C to about 100°C, alternately from about 30°C to about 40°C.

[0044] Another aspect of the invention relates to a method of etching and cleaning TiW layer including: providing a substrate comprising a TiW alloy layer and etching residues

from prior etching of the TiW layer; contacting the substrate with a solution, *e.g.*, containing hydrogen peroxide, for a time and at a temperature sufficient to cause the solution to substantially remove exposed TiW alloy; contacting the substrate with the composition according to the invention for a time and at a temperature sufficient to substantially remove the residues from the substrate; and rinsing the substrate. In one embodiment, the temperature at which the solution is used can range from about 20°C to about 100°C, alternately from about 30°C to about 40°C.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0045] FIG. 1 shows a scanning electron microscopy (SEM) image of a TiW feature on a semiconductor substrate polished using a single process etch using about 10% periodic acid for about 60 minutes at about 30°C, followed by a rinse of about 5 minutes in deionized water.

[0046] FIGS. 2A-2E show SEM images of various TiW features on a semiconductor substrate polished using a double process etch including exposure to about 35% hydrogen peroxide for about 30 minutes at about 30°C, followed by a first rinse of about 5 minutes in deionized water, followed by exposure to about 10% periodic acid for about 15 minutes at about 30°C, followed by a second rinse of about 5 minutes in deionized water.

[0047] FIGS. 3A-3D show SEM images of various TiW features on a semiconductor substrate polished using a double process etch including exposure to about 35% hydrogen peroxide for about 15 minutes at about 40°C, followed by a first rinse of about 5 minutes in deionized water, followed by exposure to about 10% periodic acid for about 15 minutes at about 40°C, followed by a second rinse of about 5 minutes in deionized water.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

[0048] Unless otherwise specified, all percentages expressed herein should be understood to refer to percentages by weight. Also, the term "about," when used in reference to a range of values, should be understood to refer to either value in the range, or to both values in the range.

[0049] Although TiW is extensively used as barrier or adhesive layer in integrated circuit fabrication, no conventional method to remove post-etch residues generated by TiW

alloy exists. Currently, best known method involves the use of hydrogen peroxide and a megasonic transducer. However, as discussed in the background, there are shortfalls associated this currently used method.

[0050] Periodic acid ("PIA"), as disclosed by U.S. Patent No. 6,117,783, is known to be effective in removing tungsten metal. Interestingly, PIA has also been found to be effective in removing etching residues following the etching of a TiW alloy. Moreover, it has been found that effective etching of TiW alloy can be obtained using PIA. The present invention is based on such findings, and presents an easy, economical and effective way of removing TiW alloy and its post-etch residues from substrate wafers.

[0051] Accordingly, one embodiment of this invention is directed to a composition comprising between 2.5% and 30% by weight of the composition of periodic acid and water, wherein the composition is effective in removing a TiW alloy and residues of etching of TiW alloy, while not removing Al, Cu, or AlCu alloy. The pH of the composition is typically less than about 7.

[0052] One aspect of this embodiment requires that the composition be substantially free of hydrofluoric acid. As used herein, the phrases "substantially no," "substantially free of," and "substantially free from," in reference to a composition means: for certain components including organic solvents, water, acids, bases, and other oxidizing agents, the aforementioned phrases should be understood to mean that the composition contains less than 1.5%, preferably less than about 1%, more preferably less than about 0.1%, of the specific element mentioned thereafter; and for other components including chelating agents, corrosion inhibitors, HF and HF salts, surfactants, and the like, the aforementioned phrases should be understood to mean that the composition contains less than 0.2%, preferably less than about 0.1%, most preferably less than about 0.01%, of the specific element mentioned thereafter. Preferably, when one of the aforementioned phrases is used, the composition is completely free of any added element specifically mentioned thereafter, or at least does not contain the added element in an amount such that the element affects the efficacy, storability, usability regarding necessary safety concerns, or stability of the composition.

[0053] Hydrofluoric acid, which is very effective in removing TiW alloy, is found to have a characteristic of attacking Al, Cu, or AlCu alloy in an equally or more effective manner, thus resulting in harmful damages in these metal layers.

[0054] In general, metals such as Al, Cu, or AlCu alloy tend to show a higher corrosion rate at higher pHs. Accordingly, in one preferred embodiment, the pH of the composition is less than about 4. In a more preferred embodiment, the pH of the composition is less than about 2.

[0055] The pH can be adjusted by using pH adjusting agents including, but not limited to: inorganic acids such as sulfuric acid, nitric acid, hydrochloric acid, and phosphoric acid; organic acids such as acetic acid, propionic acid, oxalic acid, and citric acid; ammonium; organic amine; and low-grade quaternary ammonium base. The amount of said pH adjusting agent added can be readily determined by the persons of ordinary skill in the art according to the specific components of the composition.

[0056] To be effective in removing etch residues resulting from a TiW alloy, the composition must contain an appropriate amount of PIA. It was discovered that compositions containing less than about 5% or more than about 30 % (in certain cases, more than about 20%) by weight of the composition are not effective in removing the etch residues. Accordingly, one preferred embodiment of present invention is directed to a composition which contains PIA in an amount from about 5% to about 30% by weight of the composition, alternately from about 5% to about 20% by weight. In another preferred embodiment, the invention is directed to a composition which contains PIA in an amount from about 7.5% to about 15% by weight of the composition. In yet another preferred embodiment, the composition contains PIA in an amount from about 8% to about 12% by weight of the composition. In a more preferred embodiment, the composition contains PIA in an amount of about 10% by weight of the composition.

[0057] The composition of present invention comprises PIA and water. Typically high-purity deionized water is used. Other ingredients can be included as necessary to improve the efficacy of the composition or to facilitate the use of the composition in various conditions. Examples of such ingredients include, but are not limited to, surfactants, organic solvents, abrasives, acids, bases, chelating agents, corrosion inhibitors, and other oxidizing agents such as hydrogen peroxide, hydroxylamine or its derivatives, or the like, or any combination thereof.

[0058] Examples of some organic solvents include, but are not limited to, alkyl sulfoxides such as dimethyl sulfoxide, N,N-dimethylacetamide, N,N-dimethylformamide,

and the like, and combinations thereof. In some embodiments, the compositions according to the invention may contain other organic solvents. In other embodiments, the compositions according to the invention may contain substantially no polar organic solvents.

[0059] Exemplary corrosion inhibitors include, but are not limited to, inorganic nitrate salts such as ammonium, potassium, sodium, rubidium, aluminum, zinc nitrate, or the like, compounds containing heterologous nitrogen-containing rings such as benzotriazole, and the like, and combinations thereof.

[0060] Exemplary chelating agents are described in commonly assigned U.S. Patent No. 5,672,577, issued September 30, 1997 to Lee, which is incorporated herein by reference. Preferred chelating agents include catechol, ethylenediaminetetraacetic acid or an organic or inorganic salt thereof, citric acid, glycolic acid, and combinations thereof.

[0061] Exemplary surfactants include, but are not limited to, poly(vinyl alcohol), poly(ethyleneimine), any of the surfactant compositions classified as anionic, cationic, nonionic, amphoteric, and silicone-based, and the like, and combinations thereof.

[0062] Examples of acids suitable for use in the present invention can be organic or inorganic and can include, but are not limited to, nitric, sulfuric, phosphoric, hydrochloric (though hydrochloric acid can be corrosive to metals), and the like, and combinations thereof, and/or formic, acetic, propionic, n-butyric, isobutyric, benzoic, ascorbic, gluconic, malic, malonic, glycolic, oxalic, succinic, tartaric, citric, gallic, and the like, and combinations thereof. The last five organic acids are also examples of chelating agents.

[0063] The general structure for the organic acids is as follows:  $R_1R_2-(C-X)-C(=O)-OH$ , where X can be -OH, -NHR<sub>1</sub>, -H, -Halogen, -CO<sub>2</sub>H, -CH<sub>2</sub>-CO<sub>2</sub>H, or -CHOH-CO<sub>2</sub>H; and where each of R<sub>1</sub> and R<sub>2</sub> can independently be H, an aliphatic moiety, or an aromatic moiety, or can be combined together to form a cyclic moiety.

[0064] One important factor to consider is the solubility of the acid and base products, along with any additional agents, in the aqueous solutions.

[0065] Examples of bases suitable for use to adjust the pH of the cleaning solution can include any common base(s), *e.g.*, sodium, potassium, and/or magnesium hydroxides, or the like, or a combination thereof. One major problem is that these bases can introduce mobile ions into the final formulation. Mobile ions could destroy computer chips being produced today in the semiconductor industry. Other bases can include choline salts,

bis-choline salts, tris-choline salts, ammonium hydroxide, mono-, di-, tri-, or tetra-alkylammonium hydroxides, or the like, or a combination thereof.

[0066] Another aspect of this invention is directed to a method of etching and cleaning a TiW alloy layer comprising: providing a substrate comprising an exposed TiW alloy layer; etching the TiW alloy by a method which results in formation of etching residue; contacting the substrate with a composition according to the invention for a time and temperature sufficient to cause the composition to remove at least a portion of the TiW alloy and substantially all of the etching residue from the substrate; and rinsing the substrate.

[0067] Examples of the substrate include, but are not limited to: silicone; poly-silicone; silicone oxide membrane; silicone nitride membrane; aluminum alloys such as aluminum, aluminum/copper, and aluminum/silicone/copper; titanium alloys such as titanium, titanium nitride, and titanium/tungsten; semiconductor materials such as tungsten, tantalum, and copper; compound semiconductor materials such as gallium/arsenic, gallium/phosphorus, and indium/phosphorus; and LCD materials such as a-silicone and low temperature poly-silicone.

[0068] The rinsing step can be carried out by using water soluble organic solvents, mixture of water soluble organic solvent and extra pure water, or extra pure water only.

[0069] AlCu is one of the metal alloys that are commonly included in the substrate. The composition of present invention, while very effective in removing TiW alloy and its etching residue, has little impact on AlCu alloy layer. Therefore, one embodiment of the present invention is directed to the method of removing TiW alloy and its etching residue in substrates which contain AlCu alloy layer, while leaving AlCu alloy layer intact.

[0070] The specificity of removal of the composition of the present invention with respect to TiW and AlCu can be assessed by measuring the etch rates and obtaining ratios from the etch rates. In other words, the specificity is expressed in a ratio of the composition's etch rate on TiW to its etch rate on AlCu. In a preferred embodiment, the composition has a specificity ratio of at least about 3. In a more preferred embodiment, the composition has a specificity ratio of at least about 5. In an even more preferred embodiment, the composition has a specificity ratio of at least about 7.

[0071] If the temperature at which the composition is used is too low, the composition may not achieve a sufficiently high etch rate on TiW alloy. On the other hand, if the

temperature is too high, too much etch or damage can result in the AlCu alloy layer. Accordingly, one embodiment of this invention is directed to a use of the composition to remove TiW alloy and its etching residue at a temperature ranging from about 20°C to about 100°C. In a more preferred embodiment, the composition is used at a temperature ranging from about 30°C to about 40°C.

[0072] The exfoliation time can be readily determined by the persons of ordinary skill in the art based upon factors such as the condition of resist residues and specific components to be used in the composition.

[0073] If desired, a two step process involving an etching by hydrogen peroxide followed by removing the etching residue using the composition of present invention can be employed. Therefore, another aspect of this invention is directed to a method of etching and cleaning TiW layer comprising: providing a substrate comprising a TiW alloy layer and etching residue from prior from prior etching of the TiW layer; contacting the substrate with a solution containing hydrogen peroxide for a time and temperature sufficient to cause the solution to substantially remove exposed TiW alloy; contacting the substrate with the composition of the present invention for a time and at a temperature sufficient to substantially remove the residues from the substrate; and rinsing the substrate.

[0074] Again, if the temperature at which the composition is used is too low, the composition may not achieve sufficiently high etch rate on TiW alloy. On the other hand, if the temperature is too high, too much etch or damage can result in the AlCu alloy layer. Accordingly, one embodiment of this invention is directed to a use of the composition to remove TiW alloy and its etching residue at a temperature ranging from about 20°C to about 100°C. In a more preferred embodiment, the composition is used at a temperature ranging from about 30°C to about 40°C.

## **EXAMPLES**

[0075] Certain embodiments of this invention, as well as certain advantages of this invention, are illustrated by the following non-limiting examples. Although limited number of examples are disclosed herein, it will be apparent to those skilled in the art that many modifications, both to materials and methods, may be practiced without departing from the purpose and interest of this invention.



### Example 1: Etch Rates of Various PIA Containing Compositions

[0076] Compositions containing varying amounts of PIA were prepared as specified in Table 2. The TiW substrates from Philips were etched using the compositions at a temperature and for a time denoted in Table 2. The etch rates were determined using a standard method. The results are summarized in Table 2. HF denotes hydrofluoric acid.

Table 2. Etch Rates of Various PIA-Containing Compositions

Composition	Substrate	Temp. (°C)	Time (min)	Etch Rate (Å/min)
10 % PIA	TiW	30	10	18
10 % PIA	Al/Cu	25	10	2.5
30 % PIA	TiW	35	10	32
10 % PIA + 0.06 % HF	TiW	35	10	93
5 % PIA + 0.06 % HF	TiW	35	10	150
5 % PIA + 0.06 % HF	TiW	25	10	55
2.5 % PIA + 0.06 % HF	TiW	25	10	47
2.5 % PIA + 0.06 % HF	TiW	35	10	91
2.5 % PIA + 0.06 % HF	Al/Cu	25	10	270
0.1 % HF	TiW	25	10	0.7
0.1 % HF	Al/Cu	25	10	340

[0077] As can be seen from Table 2, although the addition of HF increases the etch rate on TiW substrates, its harmful etch rate on Al/Cu alloys makes it unfavorable for the purpose of the present invention.

### Example 2: Efficacy on TiW Etching Residue Removal of Various PIA Containing Compositions

[0078] Blanket TiW wafer pieces from Philips were used as substrates. The substrates were etched and the substrates containing the etching residues were subsequently incubated with compositions containing 2.5%, 5%, 10% and 20% by weight of the

composition of PIA at 23°C for 5 to 10 minutes. The substrates were then rinsed by extra pure water, followed by nitrogen gas dry. The amount of resist residues remained upon the sample substrates was then evaluated. Evaluations were conducted by surveying the surfaces of sample substrates after treatments using a scanning electron microscope (SEM). It was determined that while the solutions containing 2.5%, 5% or 20% PIA do not effectively remove TiW etch residues, the composition containing about 10% PIA was effective in removing the TiW etch residues.

**Example 3: Determination of Removal Time**

[0079] TiW substrates were incubated with a composition containing 10% PIA at 30°C for time periods denoted in Table 3. Etching rates were determined using a standard method. The results are summarized in Table 3.

Table 3. Determination of Removal Time

Time (min)	Etch Rate (Å/min)
1	1.2
5	8.5
10	17.5
30	18.6

[0080] Although a higher etch rate is obtained from a longer incubation period, the etch rate on Al/Cu alloys also increases with time. Therefore, to achieve maximum specificity on TiW, incubation period of about 10 minutes is determined to be optimal.

[0081] It should further be apparent to those skilled in the art that various changes in form and details of the invention as shown and described may be made without departing from the spirit and scope of the invention, as claimed below.